Analysis of O_3 Formation During a Stagnation Episode in Central TN, Summer 1995

P.H. Daum, L.I. Kleinman, D. Imre,
L.J. Nunnermacker, Y.-N. Lee, S.R. Springston,
L. Newman, J. Weinstein-Lloyd, R.J. Valente,
R.E. Imhoff, R.L. Tanner, and J.F. Meagher

Environmental Chemistry Division
Brookhaven National Laboratory

Abstract

Ozone production in the Nashville urban plume during the episode that occurred on July 11 - July 13, 1995 is examined. The analysis focuses on data collected during aircraft flights on July 11. From late morning through mid-afternoon the instantaneous ozone production rate, $P(O_3)$, ranged between 10 and greater than 30 ppb/hr in the downtown area. Instantaneous production efficiencies with respect to NOx, in the downtown area, ranged between 2.5 and 8, linearly depending on the ratio of the hydrocarbon to NOx OH reactivity. Anthropogenic hydrocarbons and CO contributed about 66% of the total hydrocarbon OH reactivity in the downtown area. In the mature urban plume, downwind of Nashville, $P(O_3)$ dropped to 6 - 9 ppbv/hr at mid-afternoon, and was controlled by the availability of NOx. When present in large quantities (1 - 3 ppbv), isoprene significantly increased both the rate and efficiency of ozone production as long as the photochemical system was not strongly NOx limited.

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Introduction

In the 1995 SOS/Nashville field study, a stagnation episode occurred for the period July 11 through July 13, 1995. The highest O_3 concentration during the entire intensive (June 27 - July 20, 1995) was observed on July 12, 1995. The light daytime winds minimized transport of the urban emissions away from the city center during the daylight hours of the episode and allowed the accumulation of O_3 and O_3 precursors in near proximity to the Nashville urban center.

The weather during the stagnation period was dominated by an upper level high pressure system that moved from west to east. The weak pressure gradients of this system caused the daytime winds to be light and variable; during the daylight hours the mean boundary layer flow was less than 2 m/s throughout the episode. The mean flow was from the northeast on July 11, transporting the urban flow to the southwest of the city.

Introduction

The high pressure system also caused strong subsidence which suppressed mixing depths. These low wind speeds in combination with high humidity and solar intensity allowed the urban plume to produce very high concentrations of O_3 before it was advected out of the area.

Flights were made by one or more aircraft on each of the days during the stagnation period. On July 11, the TVA helicopter made three flights, circa 1000 - 1200, 1340 - 1530, and 1600 - 1745 local time (CDT). The helicopter flights focused on characterizing Nashville emissions and the chemical processes that occurred in the source region. The mid-morning flight included a vertical profile over the Polk Building (downtown). The DOE-G1 flew on July 11 from 1300 to 1552 CDT, and included a vertical profile to the southwest of the city. A large box pattern flown around the city, outside of the urban area, yielded data on background chemical composition. A smaller box pattern (inside the larger box) with diagonals was used to characterize the chemical composition and spatial distribution of the Nashville plume.

Measurements on July 11, 1995

The First Day of the Episode

FIGURE 1. Ground tracks of aircraft flights. Shaded area represents the approximate dimensions of the Nashville plume. Contour is drawn at an O_3 concentration of 100 ppbv. Green symbols indicate location of the hydrocarbon samples.

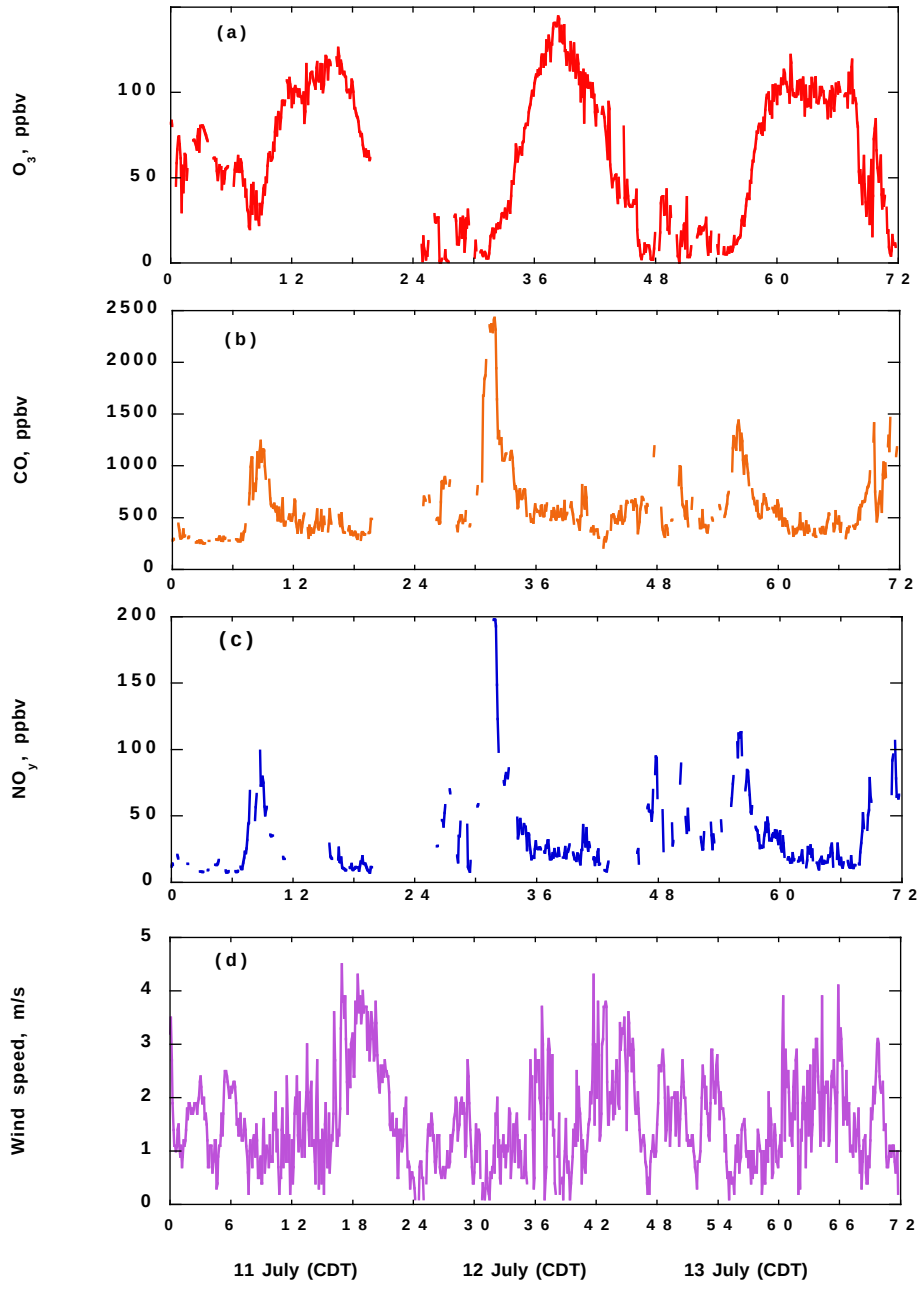

FIGURE 2. Concentrations of trace species (5 min averages) measured in downtown Nashville at the Polk Building from July 11 - July 13, 1995.

Downtown

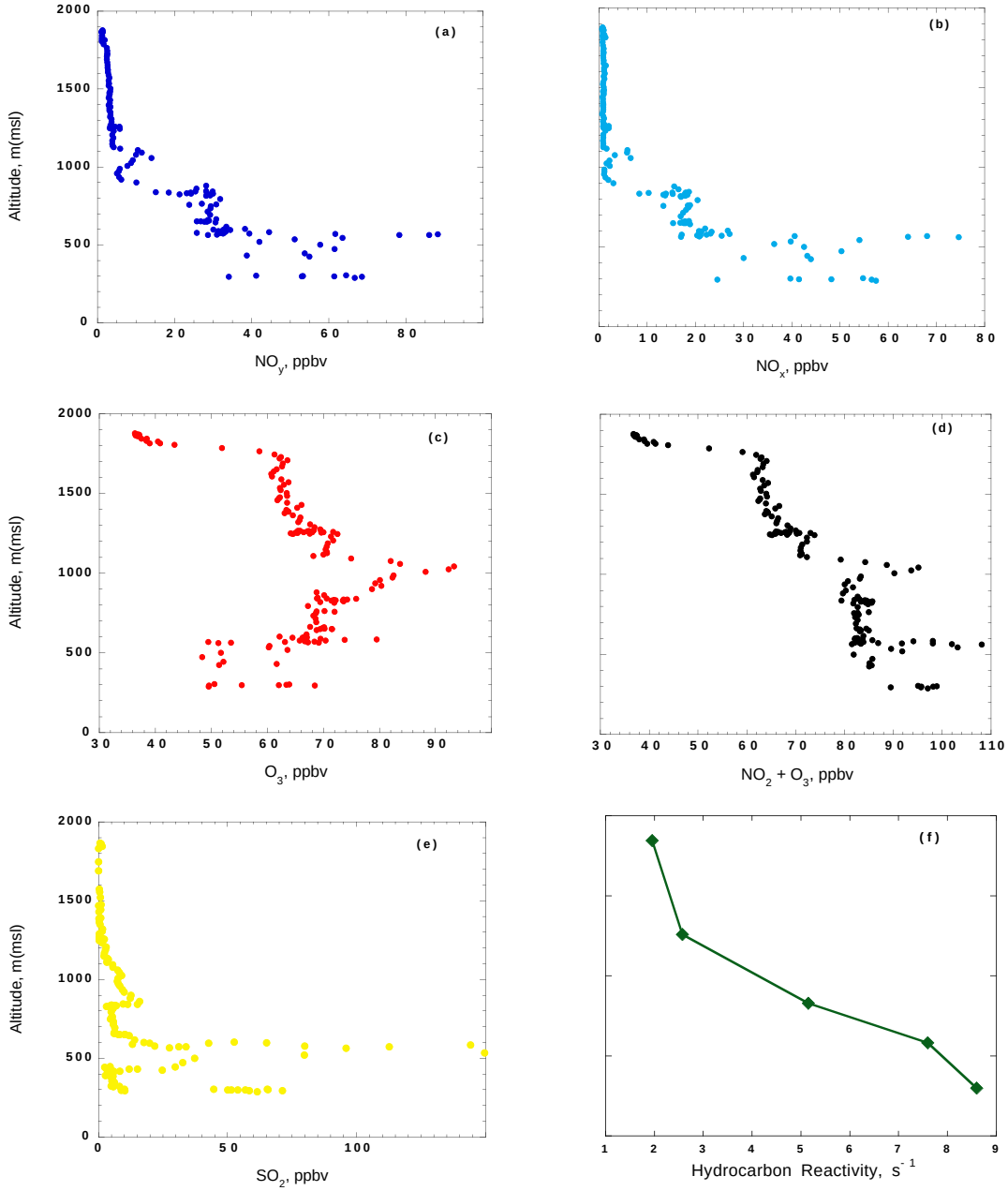

FIGURE 3. Mid-morning flight of the TVA helicopter over downtown Nashville, showing stratification in the vertical structure of the atmosphere.

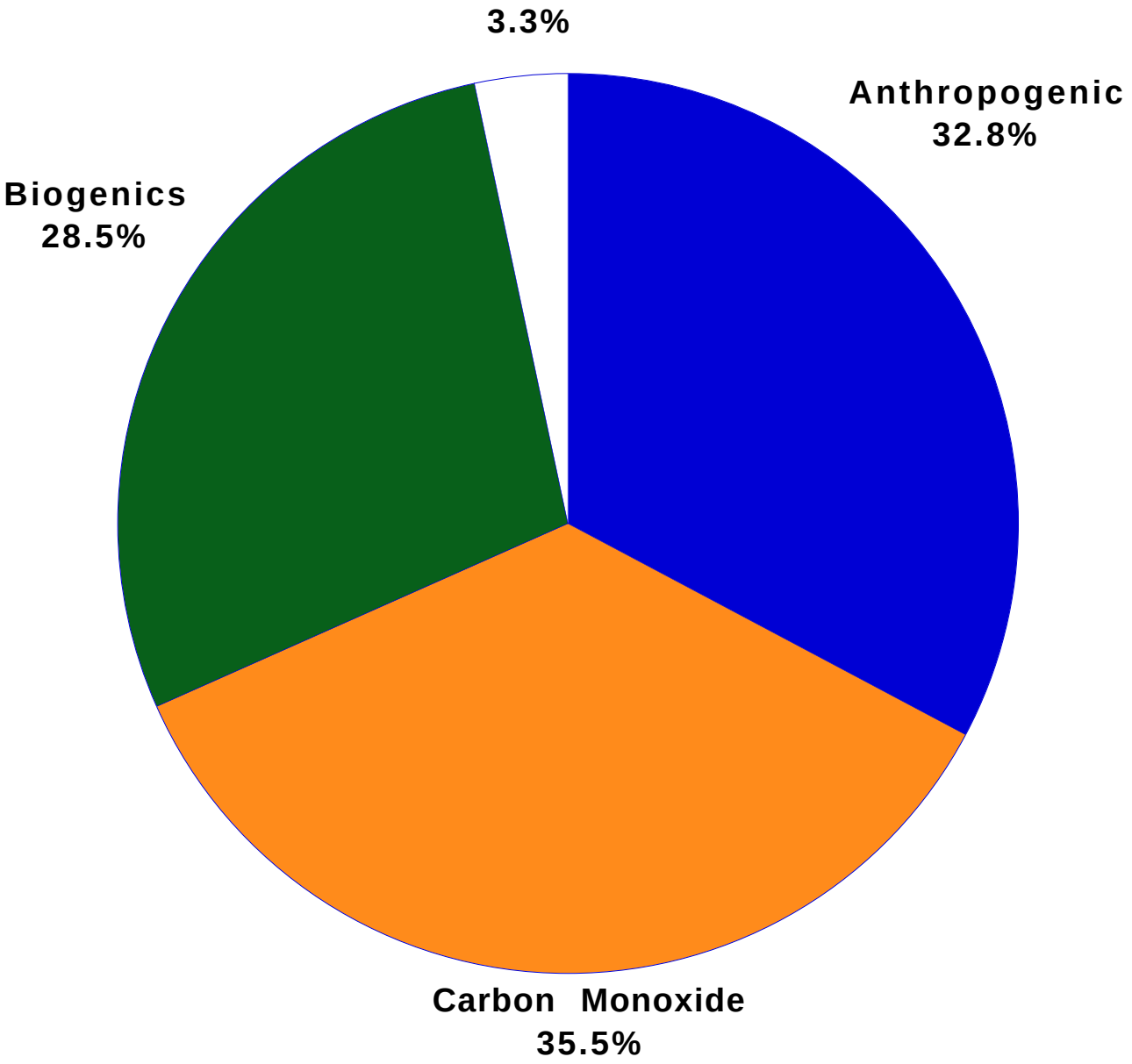

FIGURE 4. Mid-morning hydrocarbon apportionment (based on OH reactivity) in downtown Nashville. Biogenic reactivity includes contributions from isoprene, methylvinylketone, methacrolein, and 40% of the formaldehyde.

The Urban Plume

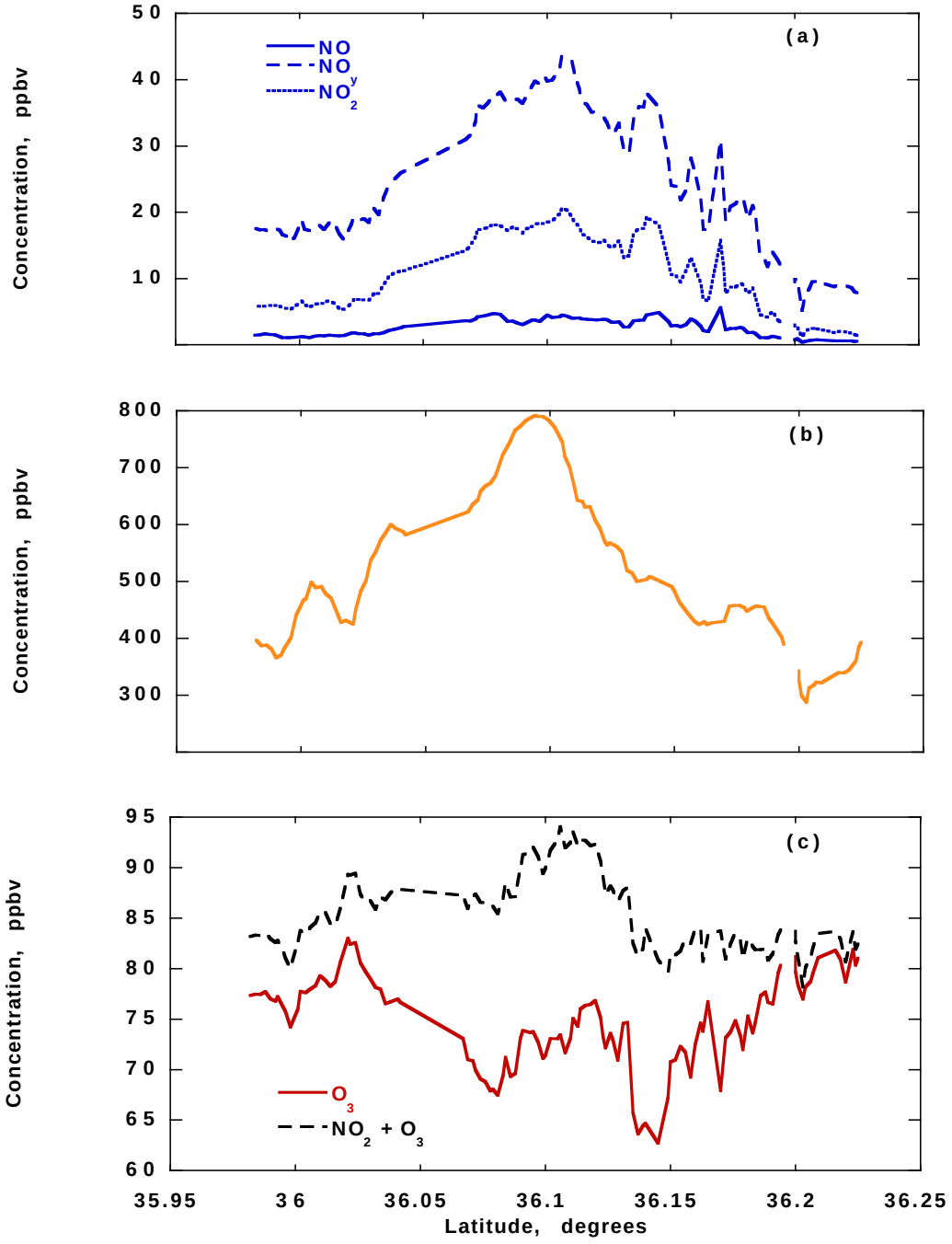

FIGURE 5. Mid-morning cross-plume trace gas concentrations measured by the TVA helicopter: a) NO, NO_2 , and NOy, b) CO, c) O_3 and $NO_2 + O_3$. Note the absence of a well-defined O_3 peak.

The Urban Plume

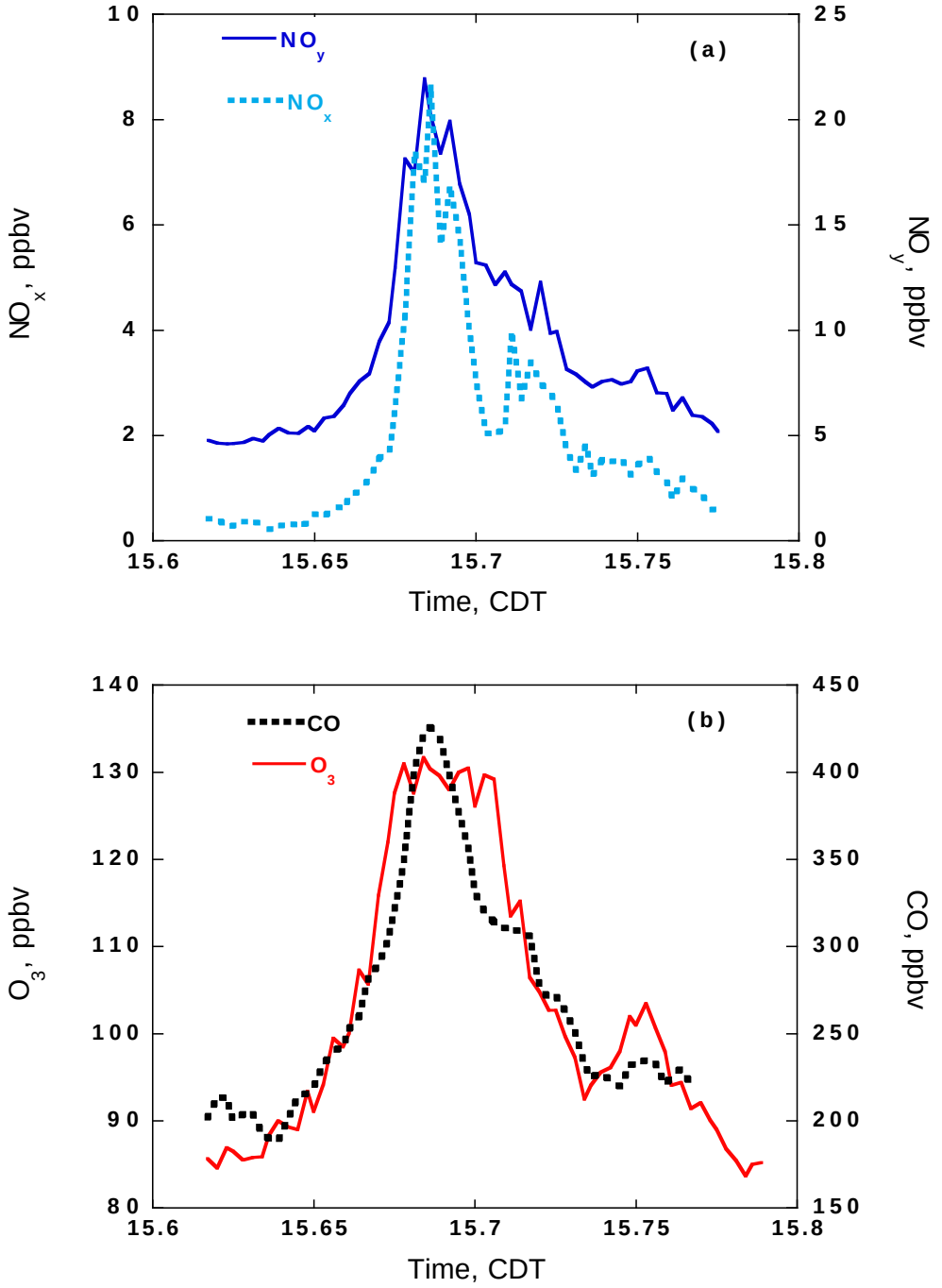

FIGURE 6. Mid-afternoon transect of the Nashville urban plume by the DOE-G1 near the center of the city. Note that although significant accumulation of O_3 has occurred, NO concentrations are still high and capable of producing additional O_3.

The Urban Plume

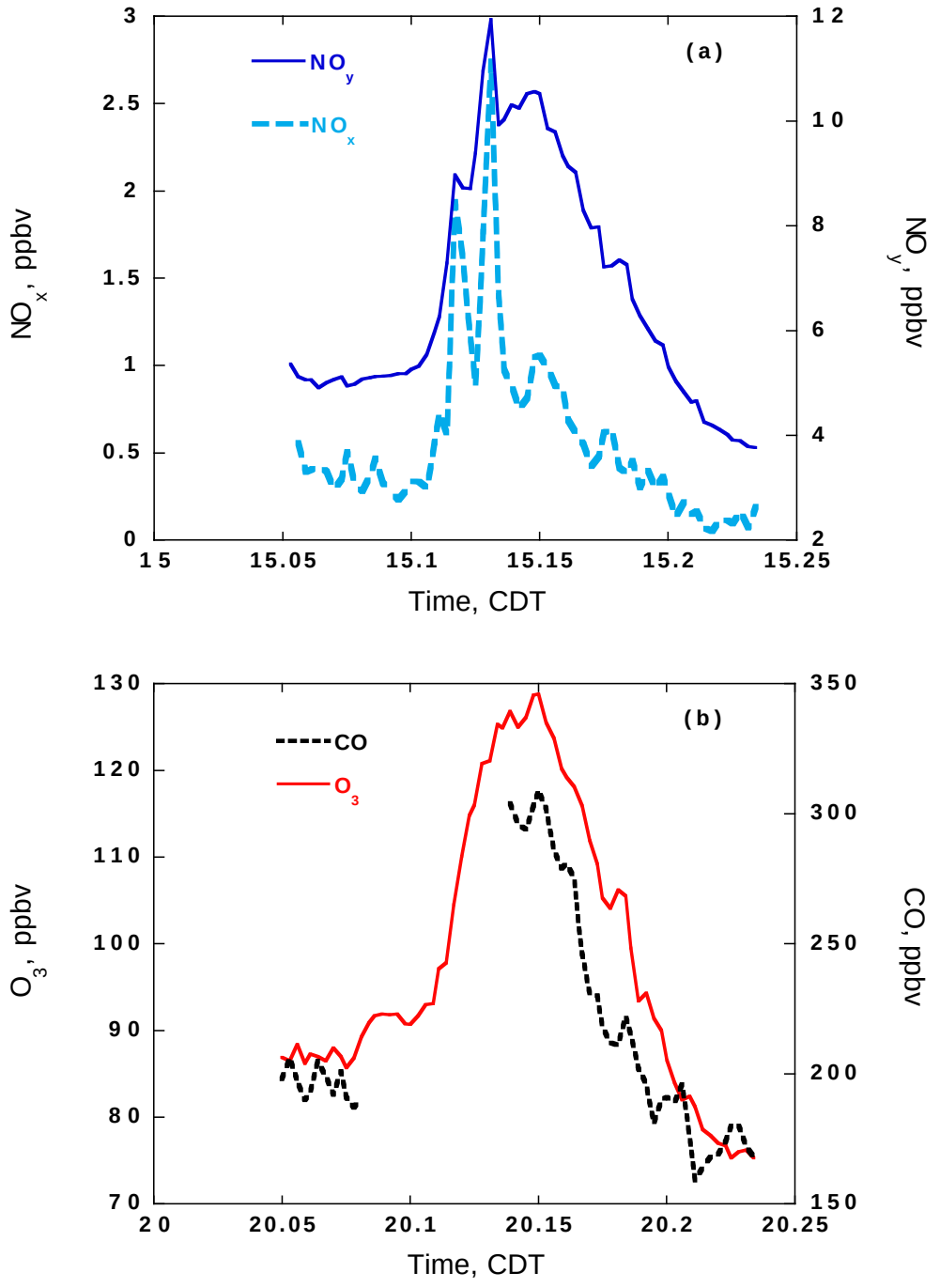

FIGURE 7. Chemical properties of the mature urban plume measured by the DOE-G1 about 30 km southwest (downwind) of Nashville.

Instantaneous Rates and Efficiencies

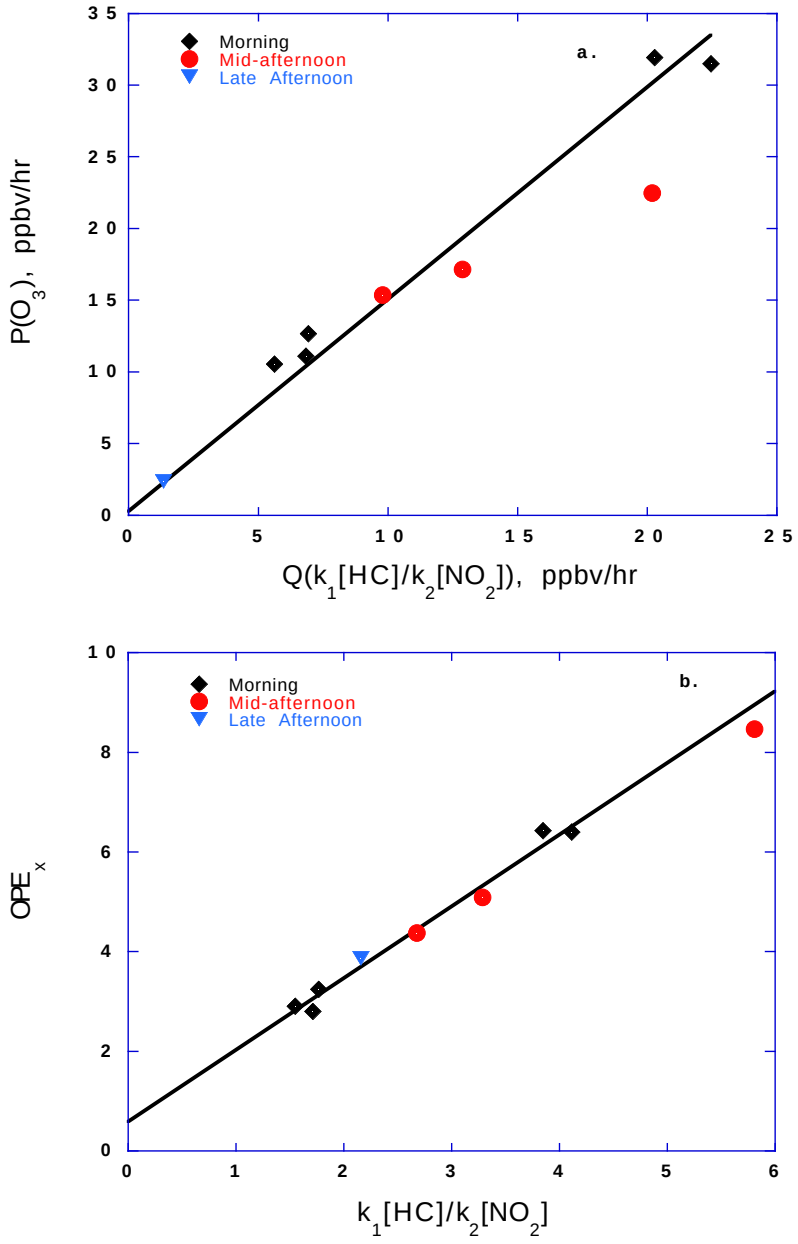

FIGURE 8. Downtown production rates and efficiencies determined for the entire day. Ozone production in the urban plume is hydrocarbon limited as indicated by the linear dependency of both $P(O_3)$ and OPEx on the ratio of the hydrocarbon to NOx OH reactivity.

Instantaneous Rates and Efficiencies

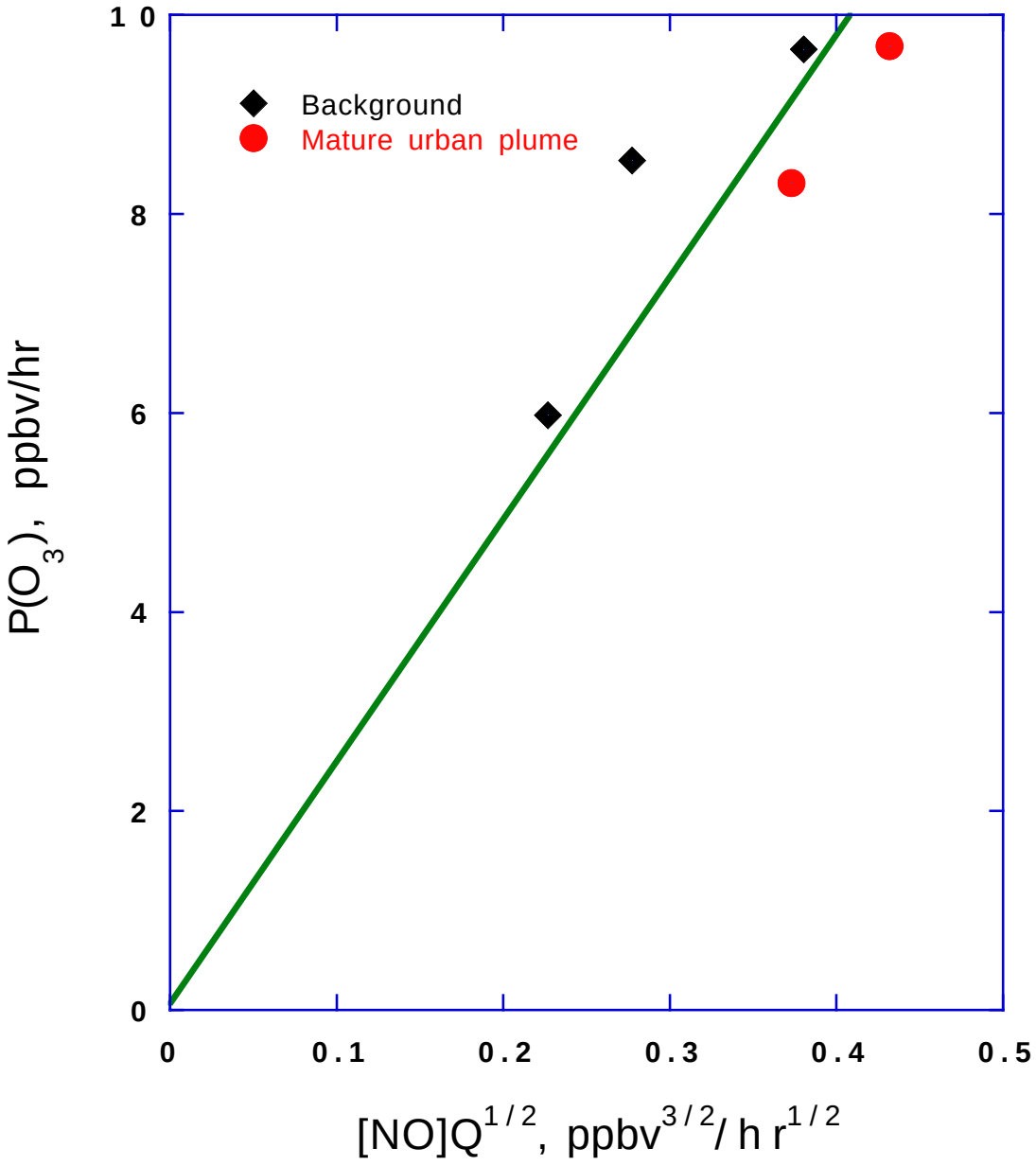

FIGURE 9. O_3 production in the mature urban plume is NOx limited, as indicated by the linear dependency of $P(O_3)$ on NO.

The Effect of Isoprene on $P(O_3)$ and OPEx

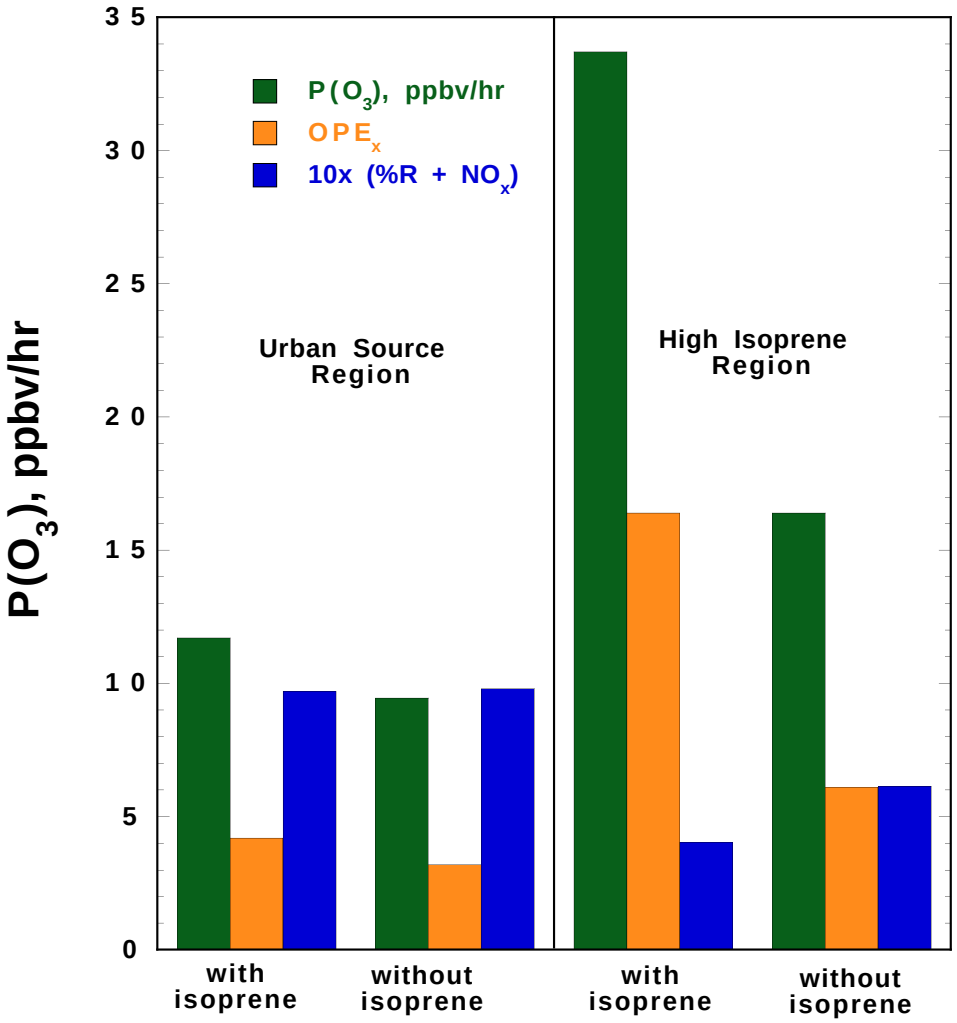

FIGURE 10. The effect of zeroing isoprene emissions on the O_3 production in the urban source region and a region of high isoprene concentrations. In the source region, $P(O_3)$ and OPEx decrease by 20% and the system is hydrocarbon limited. In the high isoprene region, $P(O_3)$ and OPEx decrease by more than a factor of 2 and shift from nominally NOx limited to hydrocarbon limited.

The Effect of Isoprene on $P(O_3)$ and OPEx

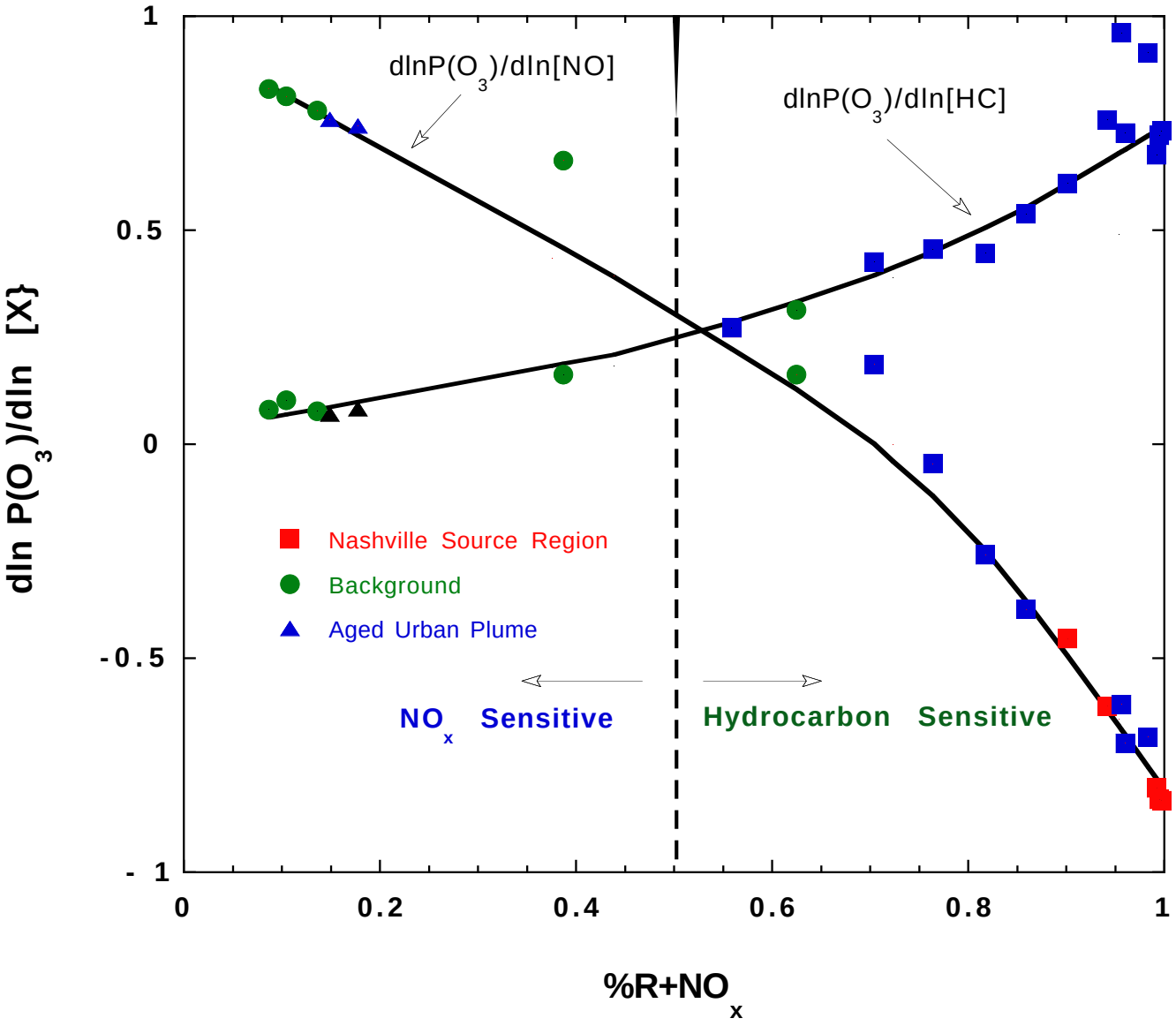

FIGURE 11. Sensitivity of $P(O_3)$ to changes in NOx and hydrocarbon concentrations. All data were collected on 7/11/95. All of the measurements in the source region exhibit hydrocarbon limited O_3 production. $P(O_3)$ in the mature urban plume is NOx limited as is $P(O_3)$ for most of the background measurements.

Conclusions

- $P(O_3)$ is limited by the availability of hydrocarbons in the urban center.

- The dominance of anthropogenic hydrocarbons in the downtown area suggests a hydrocarbon based strategy for controlling O_3 concentrations during stagnation events.

- Outside of the urban area, in the mature urban plume there is no obvious strategy for controlling O_3 concentrations.